Molecular Dynamics Study of Ionomer Structure Formation Mechanisms towards Improvement of Gas Transport Properties in PEMFC Catalyst Layers

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論 文 内 容 要 旨

Polymer electrolyte membrane fuel cells (PEMFCs) are promising power sources for automotive use. For the large-scale commercialization of PEMFC vehicles, reduction of Pt amount in catalyst layers (CLs) is indispensable to achieve an affordable price. Significant improvement of the catalytic activity has been achieved through the development of various advanced catalysts. As a significant reduction of Pt loading in CLs has come closer to reality through the improvement in catalytic activity, a limitation of reactant gas transport locally taking place in the carbon primary particle level emerges as a key challenge. However, the origin of such a large local gas transport resistance has still been controversial because of the difficulties in the measurement of structures and transport properties on an atomistic scale. Therefore, the improvement of local gas transport as a result of thorough understanding of the origin of the large local gas transport resistance and the optimum design of CLs has been strongly desired. A proton conducting ionomer is essential for proton transport, while an excess amount of ionomer inhibits the transport of reactant gases. An optimization of ionomer morphology in CLs has been recognized as a key issue for the improvement of the local gas transport, but it has been a formidable challenge because of the complexities and large number of controlling parameters in the structure formation process. Despite the many efforts to unveil the phenomena taking place during the fabrication process, the detailed mechanism of ionomer structure formation has still been elusive. In this thesis, we aim to reveal the mechanism of the ionomer structure formation during the fabrication process by a molecular dynamics simulation towards the improvement of the local gas transport in CLs.

First, the origin of the large local gas transport resistance in CLs was investigated through the development of a macroscopic mathematical model focusing on local gas transport in a single carbon primary particle. The conventional agglomerate model failed to predict the experimentally measured gas transport resistance of CLs with different effective Pt surface areas. Two local gas transport processes—gas transport through an ionomer thin film at Pt particles deposited on the surface of the carbon primary particle and gas transport through water at Pt particles deposited inside the carbon primary particle—were newly introduced in the conventional agglomerate model. The developed model showed qualitative agreement with the

experimentally measured gas transport resistance of CLs with different effective Pt surface areas. The experimental data were quantitatively reproduced by significantly reducing the gas permeability for the local gas transport processes in the vicinity of the Pt surface, which was 1/4–1/20 of the permeability measured in the bulk materials. The corrections of gas permeability were all related to the local gas transport in the vicinity of the Pt surface, which implied the presence of a high energy barrier for reactant gas transport at ionomer/Pt and water/Pt interfaces. Such a high energy barrier for the gas transport at ionomer/Pt and water/Pt interfaces could be derived from the highly dense ionomer and water structure in the vicinity of Pt surface. The parametric study with the developed model suggested that the gas transport resistance could be reduced to be about half of the original value by increasing the amount of Pt on the surface of carbon primary particles with the use of carbon with less primary pores, decreasing the ionomer thickness by reducing the ionomer content, and decreasing the average Pt radius. For the further reduction of the gas transport resistance in CLs, the improvement of the gas permeability through the ionomer is indispensable. The control of the ionomer morphology in CLs through the optimization of the fabrication process is strongly desired to improve the gas permeability through the ionomer in CLs.

Second, followed by the observation above, the structure formation of ionomer in catalyst ink was studied by molecular dynamics simulations. Ionomer adsorption at the surface of a flat graphite sheet in a solvent-saturated environment was thoroughly examined in an atomistic scale. The ionomer was adsorbed on the graphite sheet predominantly via the backbone with side chains pointing away from the graphite sheet. The amount of ionomer adsorbed on the graphite surface greatly depended on the equivalent weight (EW) of the ionomer and the alcohol content in the solvent. In the case of pure water solvent, a higher ionomer coverage was obtained when the EW of the ionomer was low. The adsorption of low EW ionomer could contribute to the reduction of the interfacial energy at the hydrophobic graphite surface by forming the thin-film structure with high density of sulfonic acid groups orienting toward the solvent. In contrast, the strong aggregation of ionomer could cause the low ionomer coverage of high EW ionomer in water-rich solvent. The coverage of low EW ionomer significantly decreased with increasing alcohol content, possibly due to the reduction of the interfacial energy at the graphite surface, improvement of ionomer dispersivity in the solvent, and increase of electrostatic repulsive interaction among dense sulfonic acid groups. The coverage of high EW ionomer increased with increasing alcohol content, then decreased at high alcohol content. The ionomer coverage at the surface with ionized functional groups was lower than that of the bare graphite surface, which indicated a significant effect of the electrostatic repulsive interaction between negatively charged functional groups and sulfonic acid groups on the ionomer adsorption. The effect of the alcohol content and EW of the ionomer on ionomer coverage still remained even in the presence of strong electrostatic interactions between sulfonic acid groups and the functionalized carbon surface. These results clearly indicate that the composition of solvent must be thoroughly tuned depending on the ionomer configuration and the surface property of carbon materials for the optimum design of the CL. However, for a further understanding of the detailed mechanism of ionomer adsorption at the carbon surface, a detailed investigation such as a free energy analysis on both ionomer adsorption at the carbon surface and dissolution into the solvent is indispensable.

Third, for a further understanding of the detailed mechanism of ionomer adsorption at the carbon surface, a dissolution free energy of an ionomer in a solvent and an adsorption free energy of an ionomer at a graphitized carbon surface were investigated using molecular dynamics simulations. The Gibbs free energy of ionomer dissolution in the solvent and ionomer adsorption at the graphite surface was calculated by integrating the free energy change of the intermediate steps generated by gradually decoupling both the Coulomb and Lennard-Jones interactions between the ionomer and the other components. The free energy difference between the intermediate steps was

calculated by the Bennett's acceptance-ratio method. The dissolution free energy of high EW ionomer in pure water solvent was considerably higher than with low EW ionomers because of the high interfacial energy due to the low surface density of sulfonic acid groups of high EW ionomer. The increase of alcohol content led to the decrease of the dissolution free energy for high EW ionomer due to the low interfacial energy derived from the high affinity of alcohol for the ionomer. In contrast, the influence of alcohol content on the dissolution free energy was small in the case of low EW ionomer. The increase in the solvation free energy of sulfonic acid groups with the increase of alcohol content due to the low dielectric constant of the solvent could compensate the decrease of the interfacial energy in the case of low EW ionomer. The lowest adsorption free energy was obtained in the case of high EW ionomer in pure water solvent because of the high dissolution free energy. The adsorption free energy increased with the increase of alcohol content in the case of high EW ionomer due to the decrease in the dissolution free energy. In contrast, in the case of low EW ionomer, the addition of alcohol lowered the free energies of the ionomer both in a solvent and at the graphite surface to the same extent, resulting in the lower dependence on the alcohol content. The estimated adsorption free energy could explain the previously calculated ionomer coverage at the graphite surface except for two extreme cases, high EW ionomer in pure water and low EW ionomer in an alcohol-rich solvent. This indicates that the ionomer adsorption at the graphite surface could be dominated by the adsorption free energy of the ionomer on the graphite sheet in most of the cases considered in the present study. The aggregation or repulsion of multiple ionomer molecules, which was not considered in the present free energy study, could dominate the structure formation in the case of high EW ionomer in pure water and low EW ionomer in an alcohol-rich solvent.

Finally, the guideline towards further reduction of the local gas transport resistance by the optimization of the fabrication parameters and the choice of materials was proposed. As proposed above, the local gas transport resistance can be reduced by increasing the amount of Pt on the surface of the carbon primary particles with the use of carbon with less primary pores. The problem of this type of the catalyst could be derived from the highly dense ionomer film adsorbed at the surface of Pt deposited outside the carbon primary particles. The formation of the dense ionomer film on Pt surface could be mitigated by the optimization of the fabrication parameters and the choice of materials. The aggregation of ionomer in the solvent could be significantly enhanced with the use of high EW ionomer and water-rich solvent, which could deny the ionomer adsorption onto Pt deposited carbon (Pt/C). The adsorption of aggregated ionomer could be further reduced by introducing the functional groups at the surface of carbon which enhances the electrostatic repulsive interaction between Pt/C and aggregated ionomer. As a result, the aggregated ionomer could be deposited in the vicinity of Pt particles with the open space instead of forming the highly dense ionomer film at the surface of Pt particles. These countermeasures are expected to reduce the ionomer coverage at Pt particles outside the carbon primary particles and result in the reduction of local gas transport resistance. Although the guideline towards the reduction of the local gas transport resistance was clearly proposed, further efforts are necessary to maximize the I-V performance by optimizing the structural and fabrication parameters through the investigation of the negative impact of the countermeasures on the other properties such as proton transport and catalytic activity.

Consequently, in this thesis, the origin of the large local gas transport resistance in CLs and the mechanism of the ionomer structure formation during the fabrication process have been studied by applying both a macroscopic model and an atomistic simulation. The multi-scale approach introduced in the present study successfully delivers the guideline towards the improvement of the local gas transport in CLs through the fundamental understanding on the mechanism of the gas transport phenomena and the ionomer structure formation in the catalyst ink. The methodology and findings could contribute to the reduction of Pt loading in CLs for the large-scale commercialization of PEMFC vehicles.

論文審査結果の要旨

固体高分子形燃料電池は次世代の動力源として期待されているが，その普及には触媒層にて用いられる白金使用量を低減しコストを下げることが必須である。低白金量条件では触媒層内における局所的な反応ガス輸送が律速となり性能低下が起こるが，その支配因子には不明な点が多く有効な解決策が打ち出せていない。特に触媒層中のアイオノマ構造は局所ガス輸送に大きな影響を及ぼすが，その構造形成機構は未だ明らかになっていない。本論文では，局所ガス輸送性向上に向けた触媒層の設計指針を得ることを目的に，マクロスケール数値モデルにより局所ガス輸送性向上に向けた課題の明確化に取り組むと共に，分子論的アプローチによりアイオノマ構造形成機構とその支配因子について検討を行っている。本論文は，これらの研究成果をまとめたものであり，全編 6 章からなる。

第 1 章は序論であり，本研究の背景と目的，および論文の構成を述べている。

第 2 章では，低白金量におけるガス輸送抵抗増大の支配因子を明確化するため，マクロスケール数値モデルによる検討を行っている。白金近傍の局所輸送過程を考慮した新たなモデルにより，従来モデルでは再現できなかった低白金量におけるガス輸送抵抗増大を正確に捉えることに成功している。また，材料の構造と使用量の最適化によりガス輸送抵抗が従来の半分以下に低減できることを示すと共に，更なる輸送抵抗低減にはアイオノマ構造の最適化が必要であることを示している。これらの結果は，低白金量におけるガス輸送抵抗増大を正確に再現する解析モデルを提供すると共に，ガス輸送性向上に向けた触媒層の設計指針とその定量的な効果を示した有用な成果である。

第 3 章では，アイオノマ構造の最適化に向けて触媒層の製造過程におけるアイオノマ構造形成の支配因子を明らかにするため，分子動力学法を用いて触媒インク中のカーボン表面におけるアイオノマ吸着構造について解析している。これにより，アイオノマの凝集構造やカーボン表面への吸着量は，アルコール濃度，アイオノマの Equivalent Weight(EW, スルホ基 1 モルあたりのアイオノマ重量)，およびカーボン表面の官能基によって制御できることを明らかにしている。特に高 EW アイオノマ，低アルコール濃度条件では特異的にアイオノマ吸着が抑制されることを示している。これらの結果は，アルコール濃度，EW，官能基の制御により，ガス輸送性向上に向けたアイオノマ構造の最適化が実現できることを示した重要な知見である。

第 4 章では，溶媒中のアイオノマ溶解自由エネルギー及びカーボン表面におけるアイオノマ吸着自由エネルギーを分子動力学法により算出することにより，アイオノマ構造形成機構について解析を行っている。溶解・吸着エネルギーは主にクーロン相互作用により決定され，溶媒とアイオノマとの接触界面構造と溶媒物性に依存することを明らかにしている。また，カーボン表面へのアイノマ吸着は，一部条件(高 EW・低アルコール濃度，低 EW・高アルコール濃度)ではアイオノマ同士の相互作用が支配因子であり，それ以外の条件では吸着自由エネルギーが支配因子であることを示している。これらの結果は，アイオノマの構造形成の支配因子に関し自由エネルギー的な見地からの解析や，それによる最適化を可能にすることを示した有用な成果である。

第 5 章では，これまでに得られた知見から，局所ガス輸送性向上に向け，触媒層材料の構造と試作条件について具体的な設計指針を提言している。これらの結果は，ミクロ~マクロスケールの計算を統合した数値解析によりメカニズム理解に基づく触媒層設計が実現できることを示した有用な成果である。

第 6 章は結論である。

以上要するに本論文は，固体高分子形燃料電池触媒層中のアイオノマ構造形成機構とその支配因子を分子論的な見地から明らかにし，局所ガス輸送性向上に向けた具体的な設計指針を提示したものであり，ナノメカニクスおよび分子流体工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。